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(54) Catalyst components for polymerization of olefins.

(57) A process for the polymerization of olefinic hydrocarbons is carried out in the presence of a catalyst comprising a catalyst component derived from reacting a compound of the formula $\text{Me}^1\text{R}^1_n\text{X}^{1-4-n}$, a compound of the formula $\text{Me}^2\text{R}^2_m\text{X}^{2-3-m}$, an organocyclic compound having two or more conjugated double bonds and a carrier of inorganic or polymeric material, and a modified organoaluminum compound having Al-O-Al bonds, the resulting polyolefins having a relatively wide molecular weight distribution, a relatively narrow composition distribution and increased bulk density.

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conium, tripropylmonochlorozirconium, tri-n-butylmonochlorozirconium, tribenzylmonochlorozirconium, dimethyldichlorozirconium, diethyldichlorozirconium, di-n-butyl-dichlorozirconium, dibenzyl-dichlorozirconium, monomethyltrichlorozirconium, monoethyltrichlorozirconium, mono-n-butyltrichlorozirconium, monobenzyltrichlorozirconium, tetrachlorozirconium, tetramethoxyzirconium, trimethoxymonochlorozirconium, dimethoxydichlorozirconium, monomethoxytrichlorozirconium, tetraethoxyzirconium, triethoxymonochlorozirconium, diethoxydichlorozirconium, monoethoxytrichlorozirconium, tetraisopropoxyzirconium, triisopropoxymonochlorozirconium, diisopropoxydichlorozirconium, monoisopropoxytrichlorozirconium, tetra-n-butoxyzirconium, tri-n-butoxymonochlorozirconium, di-n-butoxydichlorozirconium, mono-n-butoxytrichlorozirconium, tetrapentoxyzirconium, tripentoxymonochlorozirconium, dipentoxydichlorozirconium, monopentoxytrichlorozirconium, tetraphenoxyzirconium, triphenoxymonochlorozirconium, 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nium, diphenoxydibromohafnium, monophenoxytribromohafnium, tritolyloxy monobromohafnium, ditolyloxydibromohafnium, monotolyloxytribromohafnium, tribenzloxy monobromohafnium, dibenzloxydibromohafnium, monobenzloxytribromohafnium, trimethylmonoiodohafnium, triethylmonoiodohafnium, tripropylmonoiodohafnium, tri-n-butylmonoiodohafnium, tribenzylmonoiodohafnium, dimethyldiiodohafnium, diethyldiiodohafnium, dipropyldiiodohafnium, di-n-butyl diiodohafnium, dibenzyl diiodohafnium, monomethyltriiodohafnium, monoethyltriiodohafnium, monopropyltriiodohafnium, mono-n-butyltriiodohafnium, monobenzyltriiodohafnium, tetraiodohafnium, trimethoxymonoiodohafnium, dimethoxydiiodohafnium, monomethoxytriiodohafnium, triethoxymonoiodohafnium, diethoxydiiodohafnium, monoethoxytriiodohafnium, triisopropoxymonoiodohafnium, diisopropoxydiiodohafnium, monoisopropoxytriiodohafnium, tri-n-butoxymonoiodohafnium, di-n-butoxydiiodohafnium, mono-n-butoxytriiodohafnium, tripentoxymonoiodohafnium, dipentoxydiiodohafnium, monopentoxytriiodohafnium, triphenoxymonoiodohafnium, diphenoxydiiodohafnium, monophenoxytriiodohafnium, tritolyloxymonoiodohafnium, ditolyoxydiiodohafnium, monotolyoxytriiodohafnium, tribenzylloxymonoiodohafnium, dibenzyl oxydiiodohafnium, monobenzyl oxytriiodohafnium, tribenzyl monomethoxyhafnium, tribenzyl monoethoxyhafnium, tribenzyl monopropoxyhafnium, tribenzyl monobutoxyhafnium, tribenzyl monophenoxyhafnium, dibenzyl dimethoxyhafnium, dibenzyl diethoxyhafnium, dibenzyl dipropoxyhafnium, dibenzyl dibutoxyhafnium, dibenzyl diphenoxyhafnium, monobenzyl trimethoxyhafnium, monobenzyl triethoxyhafnium, monobenzyl tripropoxyhafnium, monobenzyl tributoxyhafnium, monobenzyl triphenoxyhafnium, trineophyl monomethoxyhafnium, trineophyl monoethoxyhafnium, trineophyl monopropoxyhafnium, trineophyl monobutoxyhafnium, trineophyl monophenoxyhafnium, dineophyl dimethoxyhafnium, dineophyl diethoxyhafnium, dineophyl dipropoxyhafnium, dineophyl dibutoxyhafnium, dineophyl diphenoxyhafnium, mononeophyl trimethoxyhafnium, mononeophyl triethoxyhafnium, mononeophyl tripropoxyhafnium, mononeophyl tributoxyhafnium, mononeophyl triphenoxyhafnium and the like, most preferred of which compounds are tetramethylzirconium, tetraethylzirconium, tetrabenzylzirconium, tetrapropoxyzirconium, tetrabutoxyzirconium and tetrachlorozirconium.

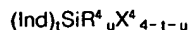
The compound (ii) used in the invention is represented by the formula $\text{Me}^2\text{R}_m^2\text{X}_{3-m}^2$ wherein R^2 is a hydrocarbon group having a carbon number of from 1 to 24, preferably from 1 to 12, more preferably from 1 to 8, including an alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, octyl, decyl and dodecyl, an alkenyl group such as vinyl and allyl, an aryl group such as phenyl, tolyl and xylyl, and an aralkyl group such as benzyl, phenethyl and styryl; X^2 is an alcoxy group of 1 - 12 carbon atoms, preferably 1 - 6 carbon atoms such as methoxy, ethoxy, propoxy and butoxy, or a halogen atom such as fluorine, iodine, chlorine and bromine; Me^2 is an element of Groups I - III in the Periodic Table; 2 is a valence of Me^2 ; and m is an integer of $0 < m \leq 3$.

Specific examples of the compound (ii) eligible for the purpose of the invention are methyl lithium, ethyl lithium, n-propyl lithium, isopropyl lithium, n-butyl lithium, t-butyl lithium, pentyl lithium, octyl lithium, phenyl lithium, benzyl lithium, dimethyl magnesium, diethyl magnesium, di-n-propyl magnesium, diisopropyl magnesium, di-n-butyl magnesium, di-t-butyl magnesium, dipentyl magnesium, methyl magnesium chloride, n-propyl magnesium chloride, isopropyl magnesium chloride, n-butyl magnesium chloride, t-butyl magnesium chloride, pentyl magnesium chloride, octyl magnesium chloride, phenyl magnesium chloride, benzyl magnesium chloride, methyl magnesium bromide, methyl magnesium iodide, ethyl magnesium bromide, ethyl magnesium iodide, n-propyl magnesium bromide, n-propyl magnesium iodide, isopropyl magnesium bromide, isopropyl magnesium iodide, n-butyl magnesium bromide, n-butyl magnesium iodide, t-butyl magnesium bromide, t-butyl magnesium iodide, pentyl magnesium bromide, pentyl magnesium iodide, octyl magnesium bromide, octyl magnesium iodide, phenyl magnesium bromide, phenyl magnesium iodide, benzyl magnesium bromide, benzyl magnesium iodide, dimethyl zinc, diethyl zinc, di-n-propyl zinc, diisopropyl zinc, di-n-butyl zinc, di-t-butyl zinc, dipentyl zinc, dioctyl zinc, diphenyl zinc, dibenzyl zinc, trimethyl boron, triethyl boron, tri-n-propyl boron, triisopropyl boron, tri-n-butyl boron, tri-t-butyl boron, tripentyl boron, trioctyl boron, triphenyl boron and tribenzyl boron.

The compound (ii) further includes an organoaluminum compound of the formulae R_3Al , R_2AlX , RAlX_2 , RAl(OR)X and $\text{R}_3\text{Al}_2\text{X}_3$ wherein R is a hydrocarbon group and X is a halogen atom, specific examples of which include trimethyl aluminum, triethyl aluminum, diethyl aluminum chloride, diethyl aluminum bromide, diethyl aluminum fluoride, diethyl aluminum iodide, ethyl aluminum dichloride, ethyl aluminum dibromide, ethyl aluminum difluoride, ethyl aluminum diiodide, tripropyl aluminum, dipropyl aluminum chloride, dipropyl aluminum bromide, dipropyl aluminum fluoride, dipropyl aluminum iodide, propyl aluminum dichloride, propyl aluminum dibromide, propyl aluminum difluoride, propyl aluminum diiodide, triisopropyl aluminum, diisopropyl aluminum chloride, diisopropyl aluminum bromide, diisopropyl aluminum fluoride, diisopropyl aluminum iodide, ethyl aluminum sesquichloride, ethyl aluminum sesquibromide, propyl aluminum sesquichloride, propyl aluminum sesquibromide, n-butyl aluminum sesquichloride, n-butyl aluminum sesquibromide, isopropyl aluminum dichloride, isopropyl aluminum dibromide, isopropyl aluminum difluoride,

silane, dicyclopentadienyldiphenyl silane, dicyclopentadienylmethylphenyl silane, dicyclopentadienylmethylchloro silane, dicyclopentadienylethylchloro silane, dicyclopentadienyldichloro silane, dicyclopentadienylmonomethoxy silane, dicyclopentadienylmonoethoxy silane, dicyclopentadienylmonomethoxymonochloro silane, dicyclopentadienylmonoethoxymonochloro silane, tricyclopentadienylmonomethyl silane, tricyclopentadienylmonoethyl silane, tricyclopentadienylmonomethoxy silane, tricyclopentadienylmonoethoxy silane and tricyclopentadienylmonochloro silane.

A further eligible compound (iii) is represented by the formula



10

wherein Ind is an indenyl group; R^4 is a hydrocarbon group of 1 - 24, preferably 1 - 12 carbon atoms including an alkyl group such as methyl, ethyl, propyl, butyl, pentyl, hexyl and octyl, an alkenyl group such as vinyl and allyl, an aryl group such as phenyl, tolyl and xylyl, and an aralkyl group such as benzyl, phenethyl, styryl and neophyl; X^4 is a halogen atom including fluorine, iodine, chlorine and bromine; and t and u are $0 < t \leq 4$ and $0 \leq u \leq 3$ respectively.

15

Specific examples of the above compound (iii) include monoindenyl silane, diindenyl silane, triindenyl silane, tetraindenyl silane, monoindenylmonomethyl silane, monoindenylmonoethyl silane, monoindenyl-dimethyl silane, monoindenyldiethyl silane, monoindenyltrimethyl silane, monoindenyltriethyl silane, monoindenylmonomethoxy silane, monoindenylmonoethoxy silane, monoindenylmonophenoxy silane, monoindenylmonomethylmonochloro silane, monoindenylmonoethylmonochloro silane, monoindenylmonomethyldichloro silane, monoindenylmonoethyldichloro silane, monoindenyltrichloro silane, bisindenyl dimethyl silane, bisindenyl diethyl silane, bisindenylmethyl ethyl silane, bisindenyl dipropyl silane, bisindenyl diphenyl silane, bisindenylmethylphenyl silane, bisindenylmethylchloro silane, bisindenylethylchloro silane, bisindenyl dichloro silane, bisindenylmonomethoxy silane, bisindenylmonoethoxy silane, bisindenylmonomethoxymonochloro silane, bisindenylmonoethoxymonochloro silane, triindenylmonoethyl silane, triindenylmonoethyl silane, triindenylmonomethoxy silane, triindenylmonoethoxy silane and triindenylmonochloro silane.

20

An inorganic carrier and/or particulate polymer carrier is used as component (iv) of the catalyst composition. The inorganic carrier may be intrinsically in the form of particles, granules, flakes, foil or fibers, but, whatever the shape may be, should be 5 - 200 μm , preferably 10 - 100 μm in maximum length. The inorganic carrier is preferably porous, having a surface area of 50 - 1,000 m^2/g and a pore volume of 0.05 - 3 cm^3 . It may be chosen from the group of a carbonaceous material, a metal, a metal oxide, a metal chloride and a metal carbonate, or a mixture thereof, which is calcined usually at 200° - 900°C in the air, nitrogen, argon or other inert gas. Suitable metals for the inorganic carrier (iii) are aluminum and nickel. Eligible metal oxides are Group I - VIII metal oxides of the Periodic Table including SiO_2 , Al_2O_3 , MgO , CaO , B_2O_3 , TiO_2 , ZrO_2 , Fe_2O_3 , $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3 \cdot \text{MgO}$, $\text{Al}_2\text{O}_3 \cdot \text{CaO}$, $\text{Al}_2\text{O}_3 \cdot \text{MgO} \cdot \text{CaO}$, $\text{Al}_2\text{O}_3 \cdot \text{MgO} \cdot \text{SiO}_2$, $\text{Al}_2\text{O}_3 \cdot \text{CuO}$, $\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3 \cdot \text{NiO}$ and $\text{SiO}_2 \cdot \text{MgO}$. The double oxides are not particularly restricted in terms of structure and component ratio when used in the invention. The metal oxides may have adsorbed thereto small quantities of moisture and may further contain a small amount of impurities.

25

The metal chloride used in the invention is a chloride of an alkaline metal or alkaline earth metal, preferably MgCl_2 and CaCl_2 . Examples of the metal carbonate are magnesium carbonate, calcium carbonate and barium carbonate, while those of the carbonaceous material referred to herein are carbon-black and activated carbon. The above metal oxides are most preferred amongst the other inorganic carrier materials.

30

The term particulate polymer as used herein as a catalyst support or carrier (iv) designates a solid particulate form of either thermoplastic or thermosetting resin having an average particle size 5 - 2,000 μm , preferably 10 - 100 μm , practically ranging from low molecular weight to ultra high molecular weight polymers as long as these polymers remain solid during the stages of catalyst preparation and polymerization reaction. Specific examples of the particulate polymer include ethylene polymers, ethylene alpha-olefin copolymers, propylene polymers or copolymers, poly-1-butene and like polyolefins preferably of 2 - 12 carbon atoms, polyester, polyamide, polyvinylchloride, polymethylacrylate, polymethylmethacrylate, polystyrene, polynorbornene and naturally occurring polymers as well as mixtures thereof. The foregoing inorganic and particulate polymer carriers may be used per se as component (iv) according to the invention. Alternatively, they may be pretreated with an organoaluminum compound such as trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, dimethylaluminum chloride, diethylaluminum chloride and diethylmonoethoxyaluminum, a modified organoaluminum compound having Al-O-Al bonds, or a silane compound.

35

The inorganic carrier may be used after treatment with an active hydrogen-containing compound such as alcohol and aldehydes, an electron-donative compound such as ester and ether, or an alkoxide-

Amongst the listed solvents are used most advantageously the aromatic hydrocarbons because the components (i), (ii) and (iii) are all soluble therein. Reference is made to the earlier mentioned procedures of pretreating the carrier materials for the utilization or disposal of the inert hydrocarbon solvents commonly used.

5 Component (ii) is used in an amount of 0.01 - 1,000 moles, preferably 0.1 - 100 moles, more preferably 1 - 10 moles per mole of component (i). Component (iii) is used in an amount of 0.01 - 100 moles, preferably 0.1 - 10 moles, more preferably 1 - 5 moles per mole of component (i). Component (i) is used in an amount by transition-metal concentration (Me) of 0.01 - 500 millimoles, preferably 0.05 - 200 millimoles, more preferably 0.1 - 20 millimoles per 100 g of carrier (iv). The catalyst components used in the invention
10 should have an atomic ratio of Al/Me¹ in the range of 0.1 - 2,000, preferably 15 - 1,000.

The term modified organoaluminum compound (II) is used herein to designate a reaction product of an organoaluminum compound and water which has 1 - 100, preferably 1 - 50 Al-O-Al bonds in the molecule. This reaction is usually conducted in the presence of an inert hydrocarbon such as pentane, hexane, keptane, cyclohexane, methylcyclohexane, benzene, toluene and xylene, of which aliphatic and aromatic
15 hydrocarbons are preferred. The starting organoaluminum compound may be represented by the formula



where R is an alkyl, alkenyl, aryl or aralkyl group having a carbon number of 1 - 18, preferably 1 - 12; X is a
20 hydrogen or halogen atom; and n is an integer of $1 \leq n \leq 3$.

The above compound is typically exemplified by trialkylaluminum having an alkyl group optionally such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, hexyl, octyl, decyl and dodecyl groups, of which methyl group is particularly preferred.

The water/organoaluminum reaction takes place in a molar ratio of water:Al in the range of 0.25:1-1.2/1, preferably 0.5:1-1/1 at a temperature of usually -70° - 100°C, preferably -20° - 20°C for a period of 5 - 24
25 hours, preferably 5 - 10 hours. As water for reaction with the organoaluminum compound, there may be used crystal water contained in hydrates of copper sulfate or aluminum sulfate.

The catalyst component (I) and the modified organoaluminum compound (II) may be supplied separately or as an admixture to the polymerization reaction system. In either case, they are used in a ratio such
30 that the atomic ratio of aluminum in the organoaluminum compound (II) to transition metal in the catalyst component (I) remain in the range of 1 - 100,000, preferably 5 - 1,000.

The term olefins as used herein designates alpha-olefins, cyclic olefins, dienes, trienes and styrene analogs. Alpha-olefins have a carbon number of 2 - 12, preferably 2 - 8 and typically include ethylene, propylene, butene-1, hexene-1 and 4-methylpentene-1. These olefins may be homopolymerized or
35 copolymerized such as by alternating, random or block copolymerization process.

The inventive process may be effectively applied where a diene compound such as butadiene, 1,4-hexadiene, ethylidene norbornene and dicyclopentadiene is used to reform the polymer product. In such a copolymerization reaction for example of ethylene and an alpha-olefin of 3 - 12 carbon atoms, it is desirable to hold an alpha-olefin content in the ethylene/alpha-olefin copolymer to 40 mole % or less, preferably 30
40 mole % or less, more preferably 20 mole % or less.

The polymerization reaction according to the invention is conducted in a slurry, solution or gas phase in the presence or absence of an inert hydrocarbon solvent such as an aliphatic hydrocarbon including hexane and heptane, an aromatic hydrocarbon including benzene, toluene and xylene, and an alicyclic hydrocarbon including cyclohexane, and methylcyclohexane, substantially without the presence of oxygen
45 and water, at a temperature of 20° - 200°C, preferably 50° - 100°C under a pressure of atmospheric -70 kg/cm²G, preferably atmospheric -20 kg/cm²G, for a time length of 5 minutes to 10 hours, preferably 5 minutes to 5 hours.

Whilst the molecular weight of the polymer product obtained may be adjusted to some extent by varying the polymerization temperature, the molar ratio of the catalyst and other polymerization parameters,
50 it can be more effectively adjusted by introducing hydrogen into the reaction system.

The inventive process can be advantageously used also in multi-stage polymerizations where hydrogen concentration and reaction temperature vary.

The invention will be further described by way of the following examples.

Preparation of Catalyst Component C

(1) Carrier (iv)

- 5 10 g SiO₂ (surface area 300 m²/g, Grade No. 952 of Fuji Davison) was used, which had been calcined at 600 °C for 5 hours. This carrier was not pretreated.

(2) Preparation of Transition Metal Catalyst Component [Components (i) + (ii) + (iii)]

- 10 A 300 cc three-necked flask was charged with 100 ml refined toluene, 25 ml tetrahydrofuran solution of n-butyilmagnesium chloride (concentration 2 mols/l) and 1.7 g cyclopentadiene and stirred at room temperature for 30 minutes, followed by addition over 20 minutes of 4.2 g tetrapropoxyzirconium dissolved in 50 ml toluene. The reaction was continued at 45 °C for 3 hours.

15 (3) Preparation of Solid Catalyst Component [Components (i) + (ii) + (iii) + (iv)]

- A 300 cc three-necked flask was charged with 10 g carrier prepared as above in nitrogen atmosphere and 29 ml toluene solution of transition metal catalyst component prepared as above, followed by addition of 15 ml refined toluene. The admixture was stirred at room temperature for 2 hours, followed by removal of
20 the solvent by nitrogen blow in vacuum thereby obtaining solid catalyst component C.

Preparation of Catalyst Component D

(1) Pretreatment of Carrier (iv)

- 25 A 400 ml stainless steel pot containing 25 pieces of half inch stainless steel balls was charged with 10 g magnesium anhydrous chloride and 3.8 g triethoxyaluminum. The admixture was subjected to ball-milling in nitrogen atmosphere at room temperature.

30 (2) Preparation of Transition Metal Catalyst Component [Components (i) + (ii) + (iii)]

- A 300 cc three-necked flask was charged with 100 ml refined toluene, 15.7 g of diethylzinc (Et₂Zn) and 5.9 g indene and stirred at room temperature for 30 minutes. 4.2 g tetrapropoxyzirconium dissolved in 50 ml toluene was added over 20 minutes. The reaction was continued at 45 °C for 3 hours.

35 (3) Preparation of Solid Catalyst Component [Components (i) + (ii) + (iii) + (iv)]

- A 300 cc three-necked flask was charged with 10 g carrier prepared as above in nitrogen atmosphere and 27 ml toluene solution of transition metal catalyst component prepared as above, followed by addition
40 of 15 ml refined toluene. The admixture was stirred at room temperature for 2 hours, followed by removal of the solvent by nitrogen blow in vacuum thereby obtaining solid catalyst component D.

Preparation of Catalyst Component E

45 (1) Pretreatment of Carrier (iv)

- 10 g polyethylene powder dried at 60 °C for 3 hours (MFR 1.0 g/10 min, bulk density 0.41 g/cc, particle size 500 μm, melting point 121 °C) was added dispersively with 6 ml toluene solution of methylalumoxane (concentration 2.5 mmol/ml). The admixture was stirred at room temperature for 1 hour, followed by drying
50 with nitrogen blow thereby obtaining a fluid particulate product.

(2) Preparation of Transition Metal Catalyst Component [Components (i) + (ii) + (iii)]

- The procedure for the preparation of Catalyst Component A was followed except that 64 ml
55 tetrahydrofuran solution of ethylmagnesium bromide (EtMgBr) (concentration 2 mols/l).

(3) Preparation of Solid Catalyst Component [Components (i) + (ii) + (iii) + (iv)]

The procedure for Catalyst Component A was followed except that the above solution of transition metal component was mixed with the above carrier (iv) such that Zr deposits were 1.9 wt%.

Preparation of Catalyst Component I

(1) Pretreatment of Carrier (iv)

The same as for Catalyst Component A.

(2) Preparation of Transition Metal Catalyst Component [Components (i) + (ii) + (iii)]

The procedure for Catalyst Component H was followed except that 4.8 g biscyclopentadienyldimethyl silane was used.

(3) Preparation of Solid Catalyst Component [Components (i) + (ii) + (iii) + (iv)]

The procedure for Catalyst Component A was followed except that the above solution of transition metal component was mixed with the above carrier (iv) such that Zr deposits were 1.9 wt%.

Preparation of Catalyst Component J - P

(1) Pretreatment of Carrier (iv)

The same as for Catalyst Component A.

(2) Preparation of Transition Metal Catalyst Component [Component (i) + (ii) + (iii)]

The transition metal catalyst components prepared are shown and identified in Table 1.

(3) Preparation of Solid Catalyst Component [Components (i) + (ii) + (iii) + (iv)]

The procedure for Catalyst Component A was followed to obtain Catalyst Components J - P having respective metal deposits as shown in Table 1.

Preparation of Catalyst Component A'

(1) Pretreatment of Carrier (iv)

A 300 cc three-necked flask was charged with 100 ml refined toluene and 10 g SiO₂ (surface area 300 m²/g, Grade No. 952 of Fuji Davison) which had been calcined at 460°C for 5 hours in nitrogen atmosphere, followed by addition of 6 ml toluene solution of methylalumoxane (concentration 2.5 mmol/ml). The admixture was stirred at room temperature for 2 hours and thereafter dried by nitrogen blow to yield a fluid particulate product.

(2) Preparation of Transition Metal Catalyst Component [Components (i) + (ii) + (iii)]

A 300 cc three-necked flask was charged with 100 ml refined toluene, 5.84 g triethylaluminum (AlEt₃) and 2.2 g indene and cooled at -60°C. A separate flask was charged with 50 ml toluene, 4.2 g tetrapropoxyzirconium (Zr(OPr)₄) and 0.8 g indene. This solution was fed into the first flask, and the whole mixture therein was stirred at -60°C for 1 hour, followed by heating with continued stirring up to 20°C slowly over 2 hours. The reaction was continued at 45°C for 3 hours until there was obtained a black solution containing 0.075 mmol/ml Zr.

Preparation of Catalyst Component E'

(1) Pretreatment of Carrier (iv)

5 A 400 ml stainless steel pot containing 25 pieces of half inch stainless steel balls was charge with 10 g magnesium anhydrous chloride and 3.8 g triethoxyaluminum. The admixture was subjected to ball-milling in nitrogen atmosphere at room temperature. 10 g milled product was used as the carrier.

(2) Preparation of Transition Metal Catalyst Component [Components (i) + (ii) + (iii)]

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The same as for Catalyst Component A'.

(3) Preparation of Solid Catalyst Component [Components (i) + (ii) + (iii) + (iv)]

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The same as for Catalyst Component A'.

Preparation of Catalyst Component F'

(1) Pretreatment of Carrier (iv)

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A 300 ml three-necked flask was charged with 100 ml refined toluene, 10 g polyethylene powder (MFR 1.0/10 min, density 0.9210 g/cm³, bulk density 0.41 g/cc, particle size 500 μ m and melting point 121 °C) and 6 ml toluene solution of methylalumoxane which was uniformly dispersed over the polyethylene powder in nitrogen atmosphere.

25

(2) Preparation of Transition Metal Catalyst Component [Components (i) + (ii) + (iii)]

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A 300 cc three-necked flask was charged with 100 ml refined toluene, 5.8 g triethylaluminum, 3g indene and 4.2 g Zr(OPr)₄ in nitrogen atmosphere at room temperature. The admixture was stirred at 45 °C for 2 hours.

(3) Preparation of Solid Catalyst Component [Components (i) + (ii) + (iii) + (iv)]

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The same as for Catalyst Component A'.

Preparation of Catalyst Component G'

(1) Pretreatment of Carrier (iv)

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The procedure for the preparation of Catalyst Component A' was followed except that silica-alumina (surface area 300 m²/g, pore volume 0.7 cc/g and average particle size 50 μ m) was used in place of silica.

(2) Preparation of Transition Metal Catalyst Component [Components (i) + (ii) + (iii)]

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A 300 cc three-necked flask was charged with 150 ml refined toluene, 15.4 g AlEt₂Cl, 4.2 g Zr(OPr)₄ and 3.4 g cyclopentadiene in nitrogen atmosphere at room temperature. The admixture was stirred at 45 °C for 2 hours.

(3) Preparation of Solid Catalyst Component [Components (i) + (ii) + (iii) + (iv)]

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The same as for Catalyst Component A'.

Preparation of Catalyst Component H'

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(1) Pretreatment of Carrier (iv)

The same as for Catalyst Component A'.

(3) Preparation of Solid Catalyst Component [Components (i) + (ii) + (iii) + (iv)]

The same as for Catalyst Component A'.

5 Preparation of Catalyst Component L'

(1) Pretreatment of Carrier (iv)

The same as for catalyst component A'.

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(2) Preparation of Transition Metal Catalyst Component [Components (i) + (ii) + (iii)]

The procedure for Catalyst Component K' was followed except that titanium tetrachloride was used in place of zirconium tetrachloride to produce TiBz₄.

15 A 300 cc three-necked flask was charged with 150 ml refined toluene, 14.6 g triethylaluminum, 5.2 g pentamethylcyclopentadiene and 5.3 g TiBz₄ in nitrogen atmosphere. The admixture was stirred at 45 °C for 2 hours.

(3) Preparation of Solid Catalyst Component [Components (i) + (ii) + (iii) + (iv)]

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The same as for Catalyst Component A'.

Preparation of Catalyst Component M'

25 (1) Pretreatment of Carrier (iv)

The same as for catalyst component A'.

(2) Preparation of Transition Metal Catalyst Component [Components (i) + (ii) + (iii)]

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The procedure for Catalyst Component K' was followed except that hafnium tetrachloride was used in place of ZrBz₄ to produce HfBz₄.

A 300 cc three-necked flask was charged with 150 ml refined toluene, 14.6 g triethylaluminum, 2.54 g cyclopentadiene and 5.8 g ZrBz₄. The admixture was stirred at 45 °C for 2 hours.

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(3) Preparation of Solid Catalyst Component [Components (i) + (ii) + (iii) + (iv)]

The same as for Catalyst Component A'.

40 Preparation of Catalyst Component N'

(1) Pretreatment of Carrier (iv)

The procedure for Catalyst Component A' was followed except that 15 ml hexane solution of Zr(OPr)₄ - (concentration 1 mmol/ml) was used in place of methylalumoxane.

45

(2) Preparation of Solid Catalyst Component [Components (i) + (ii) + (iii) + (iv)]

A 300 cc three-necked flask was charged with 10 g carrier prepared as above, 100 ml refined n-hexane, 0.84 g triethylaluminum and 0.12 g cyclopentadiene. The admixture was stirred at room temperature for 2 hours, followed by addition of 0.5 g Zr(OEt)₄, and thereafter stirred at 45 °C for 2 hours in nitrogen atmosphere. The solvent was removed by nitrogen blow in vacuum.

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Table 2 shows the polymerization results and the properties of resultant polymers (Inventive Examples 1 - 18 and Comparative Examples 1 - 3).

Inventive Examples 20 - 35

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The procedure of Inventive Example 19 was followed that Catalyst Components B' - O' were used in place of Catalyst Component A' as indicated in Table 3.

Comparative Examples 4 - 6

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The procedure of Inventive Example 19 was followed except that Catalyst Components T, U and V were used in place of Catalyst Component A'.

Table 4 shows the polymerization results and the properties of resultant polymers (Inventive Examples 19 - 35 and Comparative Examples 4 - 6).

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Each of the polymers obtained in the respective Inventive and Comparative Examples was subjected to the following tests.

Melt Index (MI)

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The procedure of ASTM D1238-57T was followed.

Density (D)

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The procedure of ASTM D1505-68 was followed.

Melting Point by Calorimetry (DSC)

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5 mg of the polymer sample was disposed at 180 °C for 3 minutes, cooled to 0 °C over 10 °C/min and allowed to stand at 0 °C for 10 minutes, followed by heating with a temperature rise of 10 °C/min with use of a melting point tester (Seiko Electronics DSC-20).

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Table 1 (cont'd)

	Catalyst lot	solid catalyst component				composition ratio (i):(iii):(ii) mol ratio	transi- tion metal deposits wt%	amount of addition during polymerization		Al/Me ratio
		carrier (iv)	component (i)	component (iii)	compo- nent (ii)			transition metal mg	modified Al	
IE 11	K	SiO ₂ -MAO	Ti(OnBu) ₃ Cl	cyclopentadiene	EtMgCl	1 : 3 : 10	2.0	2.3	MAO	1000
12	L	"	ZrBz ₄	"	"	1 : 4 : 8	"	1.9	"	"
13	M	"	Zr(neophil) ₄	pentamethyl- cyclopentadiene	"	"	"	1.7	"	"
14	N	"	ZrCl ₄	cyclopentadiene	EtLi	1 : 2 : 6	"	2.1	"	"
15	O	"	TiCl ₄	"	EtMgCl	1 : 2 : 4	"	2.0	"	"
16	P	"	Hf(OPr) ₄	"	"	1 : 4 : 8	"	2.4	"	"
17	H	"	Zr(OEt) ₄	bis-indenyl- ethane	"	1 : 2 : 4	1.9	1.8	"	"
18	H	"	"	"	"	"	"	"	"	"
CE 1	Q	-	Zr(OPr) ₄	indene	EtMgCl	1 : 4 : 8	-	1.7	"	"
2	R	SiO ₂ -MAO	"	-	"	1 : 0 : 7	2	1.6	"	"
3	S	"	"	indene	-	1 : 4 : 0	"	1.5	"	"

IE : Inventive Example CE : Comparative Example

Table 3

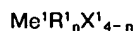
	Catalyst lot	solid catalyst component				composition ratio (i):(ii):(iii) mol ratio	transition metal deposits wt%	amount of addition during polymerization transition metal mg	Al/Me ratio
		carrier (iv)	component (i)	component (iii)	component (ii)				
IE 19	A'	SiO ₂ -MAO	Zr(OPr) ₄	indene	AlEt ₃	1 : 2 : 4	2	2	MAO 1000
20	B'	"	"	cyclopentadiene	"	"	1.5	"	"
21	C'	SiO ₂	"	"	AlEt ₂ (OEt)	1 : 4 : 8	"	1.8	"
22	D'	Al ₂ O ₃ -MAO	Zr(OBu) ₄	methylcyclopentadiene	AlEt ₃	1 : 2 : 4	1.8	1.7	"
23	E'	MgCl ₂ -Al(OEt) ₃	Zr(OPr) ₄	indene	"	"	2.0	1.8	"
24	F'	PE polymer-MAO	"	"	"	"	"	1.9	"
25	G'	SiO ₂ -Al ₂ O ₃ -MAO	"	cyclopentadiene	AlEt ₂ Cl	1 : 4 : 10	"	1.7	"
26	H'	SiO ₂ -MAO	Zr(OEt) ₄	bis-cyclopentadienyl-dimethyl silane	AlEt ₃	1 : 2 : 4	"	1.6	"
27	I'	"	Zr(OPr) ₄	bis-cyclopentadienyl-methane	"	"	"	1.9	"
28	J'	SiO ₂ -AlMe ₃	Zr(OPr) ₃ Cl	bis-indenyl-ethane	"	1 : 4 : 8	"	1.8	"

Table 4

		yield g	catalytic activity g/gMe	MFR g/10 min	bulk density g/cc	polymer density g/cm ³	melting point ° C
5	IE 19	76	38,000	0.9	0.38	0.9221	114.1
	20	98	49,000	3.8	0.40	0.9215	104.5
	21	57	32,000	4.3	0.41	0.9228	105.1
	22	73	43,000	2.8	0.39	0.9233	106.3
10	23	67	37,000	0.7	0.30	0.9218	113.8
	24	76	40,000	0.8	0.33	0.9233	114.5
	25	86	51,000	3.5	0.40	0.9235	106.5
	26	61	38,000	2.3	0.41	0.9229	105.3
15	27	44	23,000	4.5	0.38	0.9217	104.8
	28	95	53,000	0.9	0.40	0.9215	107.3
	29	73	43,000	6.2	0.36	0.9217	105.1
	30	66	35,000	1.1	0.35	0.9234	98.0
20	31	72	29,000	2.9	0.39	0.9236	106.4
	32	97	61,000	1.5	0.42	0.9510	135.1
	33	99	37,000	1.9	0.37	0.9054	139.7
	34	94	52,000	8.0	0.37	0.9218	105.7
25	35	47	25,000	0.1	0.31	0.9219	113.9
	CE 4	95	56,000	0.08	0.20	0.9196	113.0
	5	0	0	-	-	-	-
	6	17	11,000	1.3	0.40	0.9280	115.8
IE : Inventive Example CE : Comparative Example							

30 Claims

1. A process for the manufacture of polyolefins which comprises polymerizing a wide range of olefinic hydrocarbons in the presence of a catalyst composition characterised in that said catalyst composition comprises a first component (I) and a second component (II),
 35 said first component (I) resulting from the reaction of a compound (i) of the formula



- 40 wherein R¹ is a hydrocarbon moiety of 1 - 24 carbon atoms, X¹ is a halogen atom, Me¹ is a metal of the group of zirconium, titanium and hafnium, and n is an integer of 0 ≤ n ≤ 4;

A compound (ii) of the formula



- 45 wherein R² is a hydrocarbon group of 1 - 24 carbon atoms, X² is an alkoxy group of 1 - 12 carbon atoms or a halogen atom, Me² is an element of I - III Groups in the Periodic Table, z is a valence, and m is an integer of 0 < m ≤ 3;

- 50 an organocyclic compound (iii) having two or more conjugated double bonds; and an inorganic carrier and/or particulate polymer carrier (iv),
 said second component (II) being a modified organoaluminum compound having Al-O-Al bonds derived from the reaction of an organoaluminum compound and water.

- 55 2. A process as claimed in Claim 1 characterised in that said compound (ii) is an organoaluminum compound of the formulae



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atoms or a halogen atom, Me^2 is an element of I - III Groups in the Periodic Table, z is a valence, and m is an integer of $0 < m \leq 3$;

an organocyclic compound (iii) having two or more conjugated double bonds; and
an inorganic carrier and/or particulate polymer carrier (iv),

5 said second component (II) being a modified organoaluminum compound having Al-O-Al bonds derived from the reaction of an organoaluminum compound and water.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 31 0315

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 260 130 (EXXON) * Claims; page 10, lines 10-64; page 8, line 54 - page 9, line 18; page 4, lines 4-6; page 9, lines 34-48 *	1,2,3,6	C 08 F 4/642 C 08 F 10/00
X	EP-A-0 447 071 (BP CHEMICALS) * Claim 7 *	1,2,3	
A	DE-A-1 720 785 (HOECHST)		
A	US-A-5 021 382 (G.D. MALPASS, Jr.)		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 F
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		23-03-1993	DE ROECK R G O
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone V : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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